Corrosion of Heat Exchanger Alloys in sCO_2 Power Cycles

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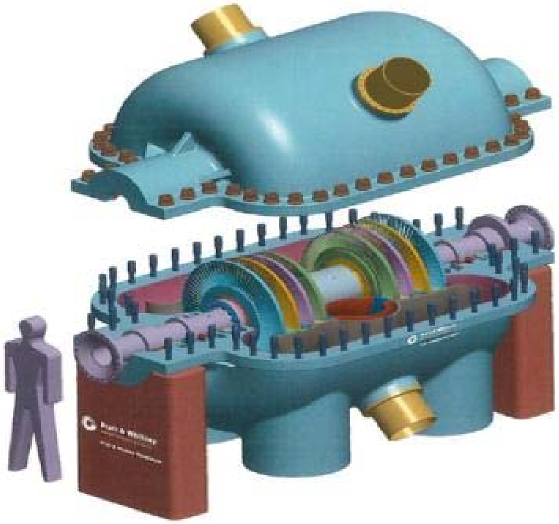
Objectives

- *Corrosion database*
  - *determine performance of structural alloys in laboratory high-temperature high-pressure supercritical CO_2 (sCO_2)*
- *Computational model development*
  - *build on an existing EPRI Oxide Exfoliation Model*
    - *Includes laboratory data and configurations pertaining to sCO_2 heat exchangers and recuperators*



sCO_2 Power Turbine (676 MW)

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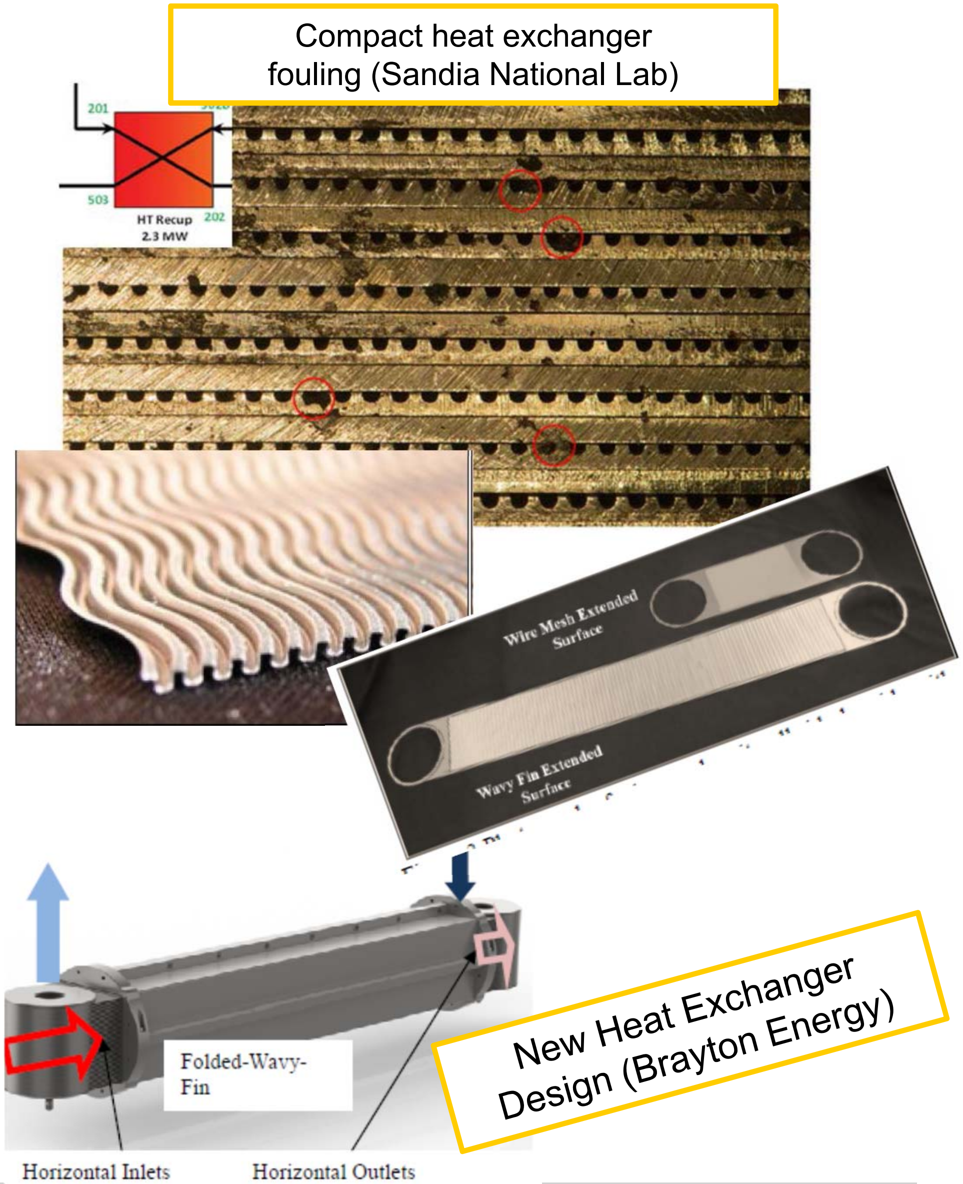
Materials selection to help DOE achieve Supercritical Transformational Electric Power (STEP) program

Technology challenges for sCO_2 HX

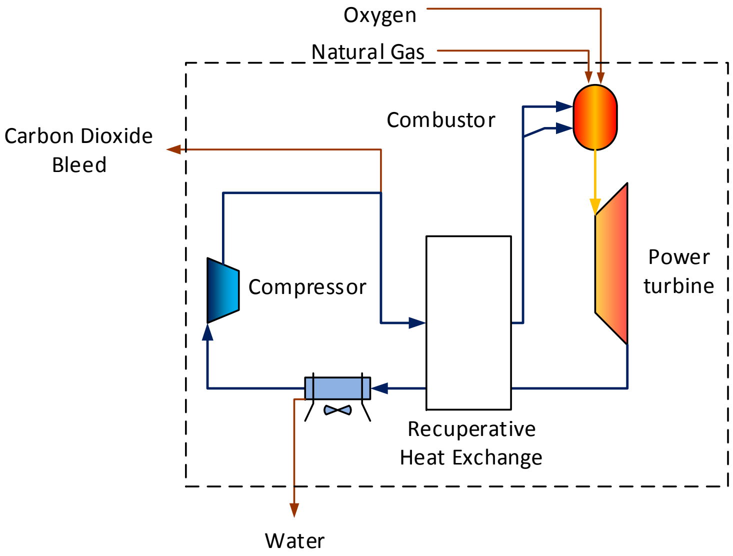
- 4-10X heat duty compared to Rankin Cycle
- HX Expensive: ~40% of total plant cost
- Unique designs
  - – *small channels*
  - – *large surface areas*
- Materials considerations
  - – *Mechanical:*
    - *thermal fatigue, creep (thin-wall structures)*
  - – *Manufacturing:*
    - *brazing/diffusion bonding*
  - – ***Corrosion:***
    - ***oxidation, carburization, exfoliation, pluggage, etc.***


Compact heat exchanger fouling (Sandia National Lab)

New Heat Exchanger Design (Brayton Energy)

Realistic sCO_2 conditions simulated in lab for Allam cycle

- **Survey of industry and literature data**
  - *700°C likely maximum temperature for heat exchangers*
- **Evaluation of impurities for near-term ‘open/direct-fired cycle’ – Allam Cycle**
  - *H_2O, O_2, N_2, Ar, NO_x, SO_x, HCl*
  - *thermodynamic and mass-balance calculations for methane (NG) and cooled coal syngas*



Species	Composition (mol%)		
	Methane	Cooled raw coal syngas	Oxygen
CH_4	100	1.0	
CO		39.0	
H_2		28.3	
CO_2		8.0	
H_2O		20.0	
N_2+Ar		2.0	0.5
H2S	2 ppm	0.9	
HCl		0.02	
O_2			99.5
LHV	912 BTU/scf	218 BTU/scf	

Component	Composition (mol%)			
Fuel Stream	Methane		Cooled Raw Coal Syngas	
	Combustor Inlet	Turbine Inlet	Combustor inlet	Turbine Inlet
CO_2	95	90	90	85
H_2O	250 ppm	5.3	250 ppm	5
N_2+Ar	1	1	9	9
O_2	3.8	3.6	1	1
HCl				20 ppm
SO_2				1,000 ppm

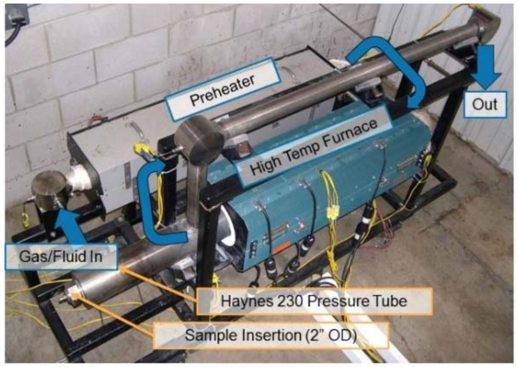
3.6 mol% O_2, 5.3 mol% H_2O

Scope of laboratory sCO_2 corrosion study

- Alloys
  - *commercially available*
  - *code approved/industry relevant*
  - *focus on economics*

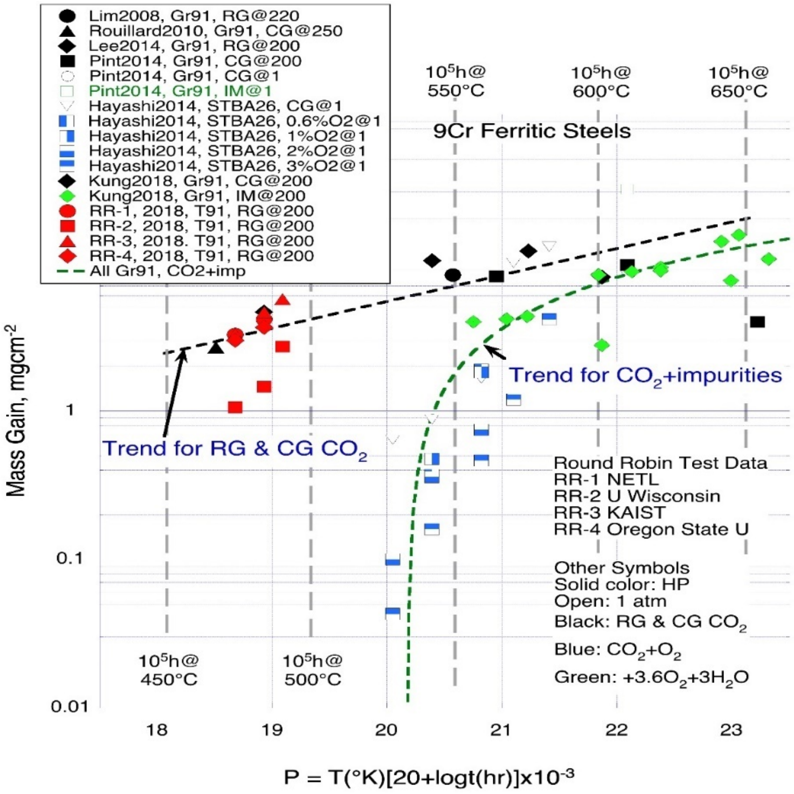
Material Class	Alloys Selected		
Ferritic steels	**Gr 91** (8-9Cr)	**VM12** (11-12Cr)	**Crofer 22H** (20Cr)
Austenitic stainless	**TP304H** (18Cr)	**HR3C** (25Cr)	
Nickel-based	**IN617** (20Cr, solid solution strengthened)	**IN740H** (25Cr, ppt. strengthened)	

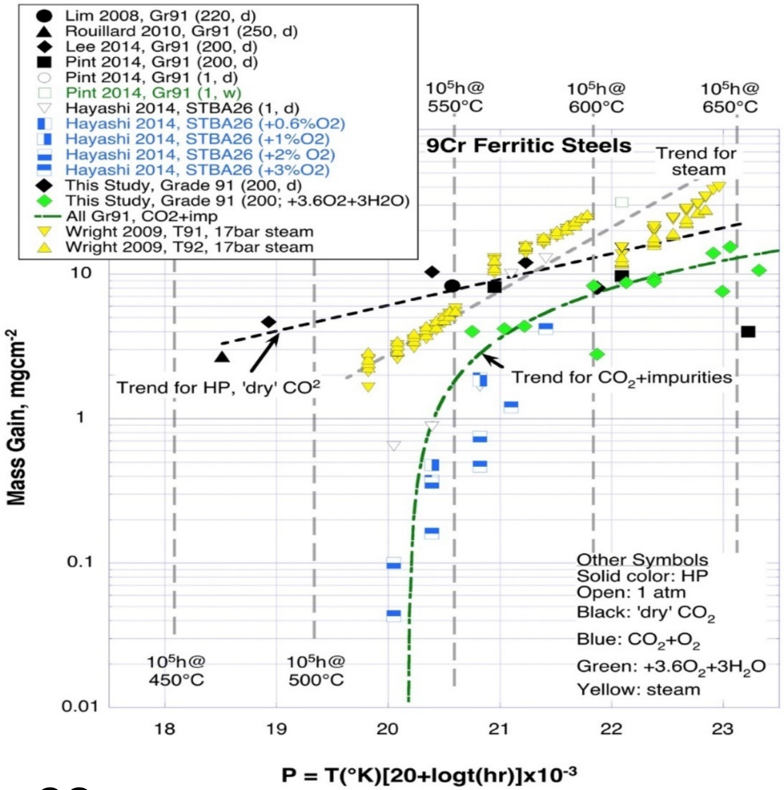
- Conditions
  - *650-750°C, 200 bar*
  - *sCO_2*
    - commercially pure CO_2
    - impure CO_2 (with O_2 + H_2O) - to simulate semi-open cycle in NG oxy combustion



- Exposures
  - *2 x 300-h shakedown tests in CO_2 ± impurities, 700°C, 200 bar (Gr91, TP304H, IN740H)*
  - *3 x 1,000-h tests in CO_2 + impurities, 650, 700, 750°C, 200 bar (all 7 alloys)*
  - *1 x 5,000-h test in CO_2 + impurities, 700°C, 200 bar (all 7 alloys)*

Group 1
Ferritic steels: available mass-gain data in CO_2

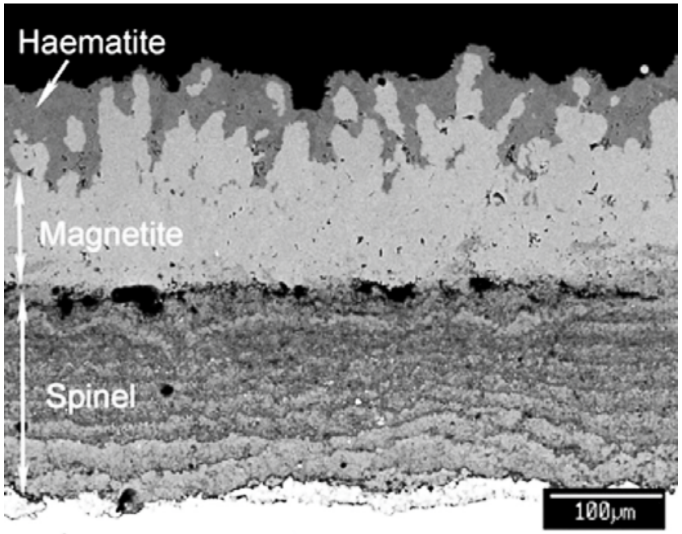




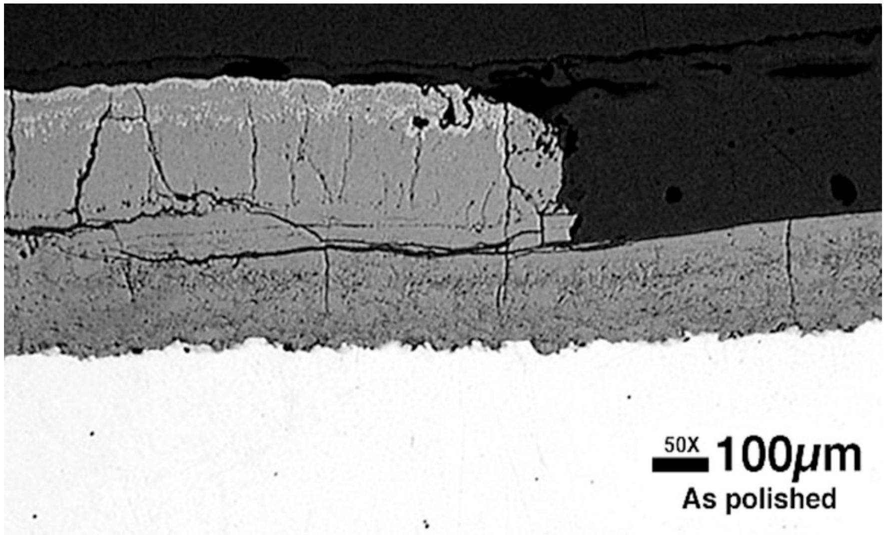
- Pure CO_2
  - *mass gains similar to those in steam at higher values of Larson-Miller parameter* (*P*)
- Impure CO_2
  - *significantly lower mass gains than in pure CO_2 at lower values of P*
- Expect similar morphologies in sCO_2 and steam at higher T and/or longer time

EPRI supplied samples to all sCO_2 Round Robin testing labs and provided technical support in kind

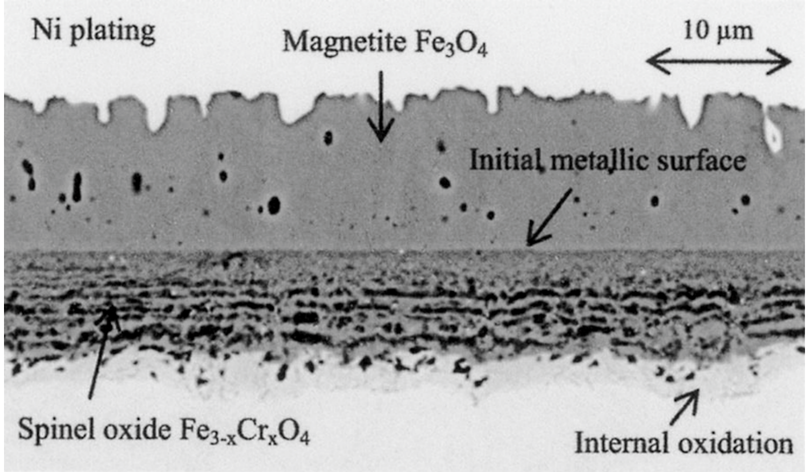
Group 1
Typical scale morphologies formed on ferritic steels



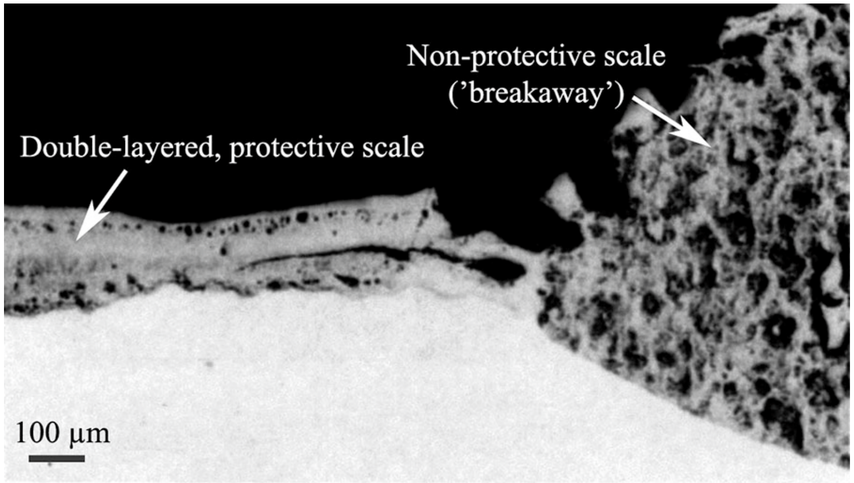
T91, 64kh at 566°C & 138 bar steam (EPRI Atlas)



T91, 155kh at 538°C & 17 bar steam (EPRI Atlas)

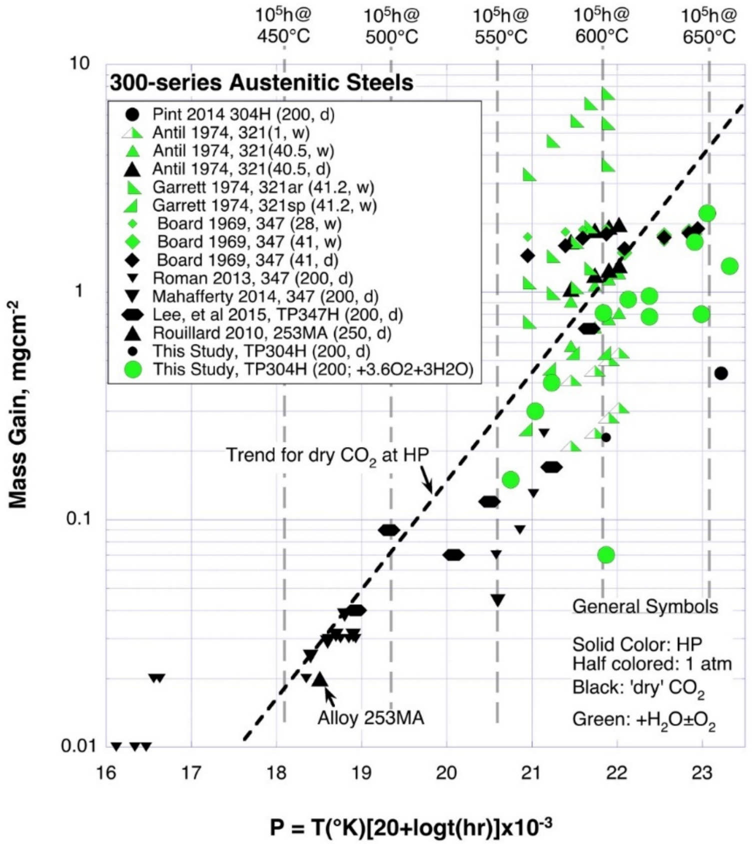


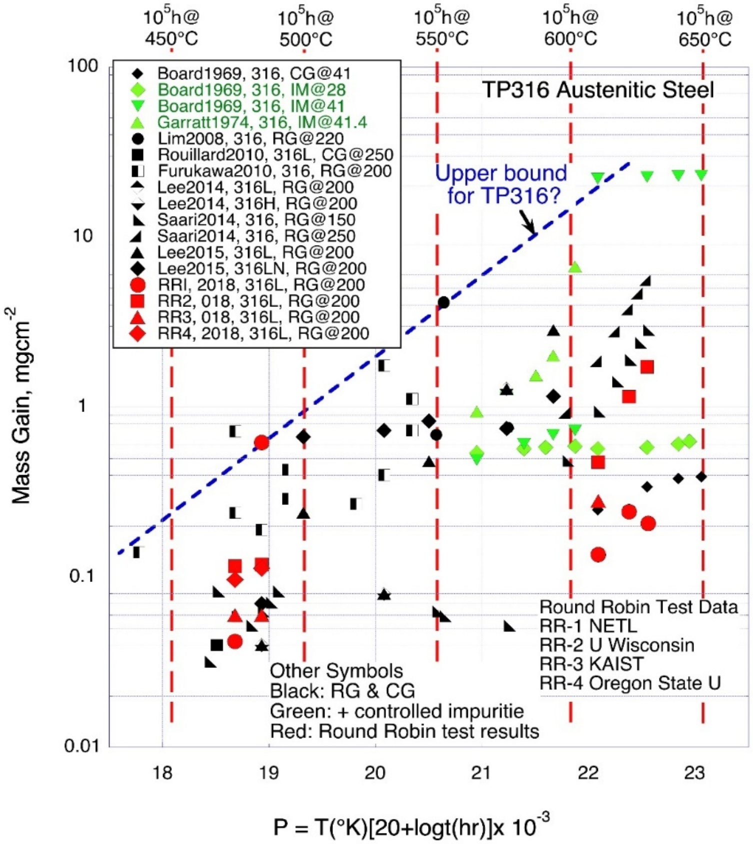
T91, ≈300h at 550°C & 250 bar CO_2 (Rouillard, 2010)



Fe-9Cr, ≤9kh at 550°C & 40 bar (imp) CO_2 (Harrison, 1974)

Group 2
Austenitic stainless steels: available mass-gain data in sCO_2



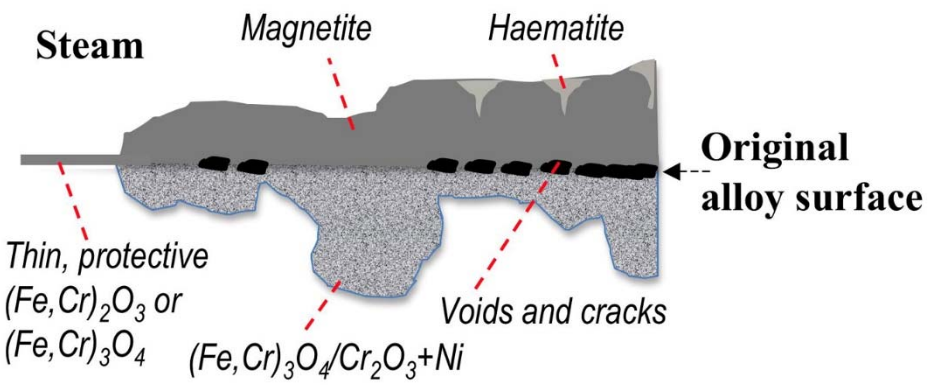


- Considerable data scattering
- No real trend for pure vs. impure CO_2

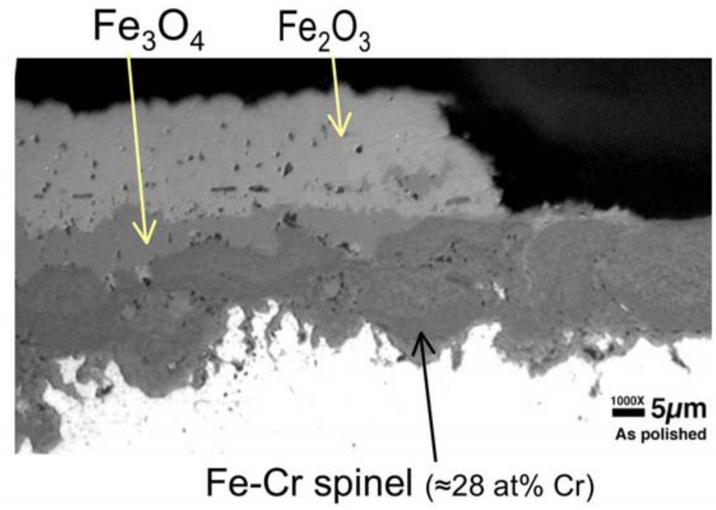
  -or for HP vs. 1 atm.

  -or vs. HP steam (not shown)
- Expect similar morphologies in sCO_2 ± most impurities, and HP steam

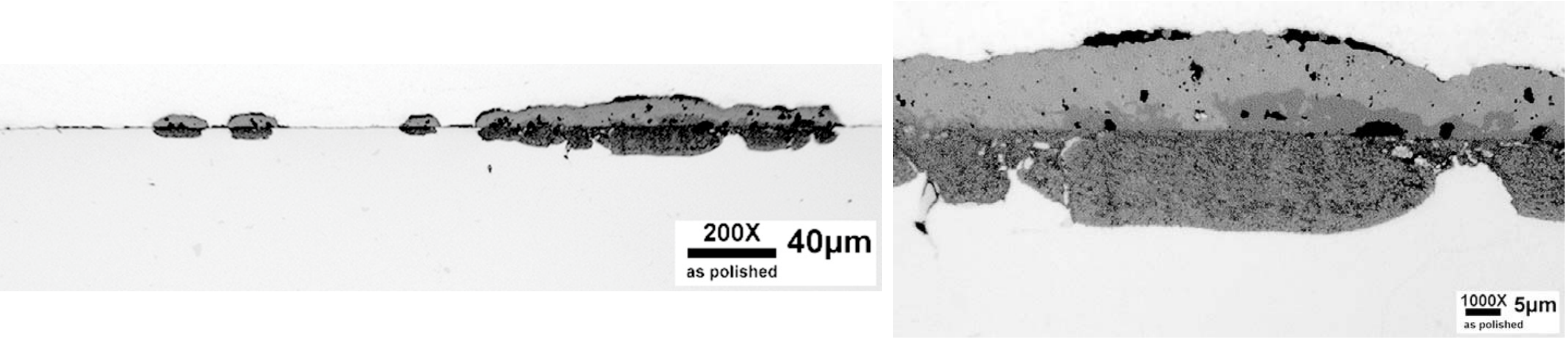
Group 2
Typical scale morphologies on austenitic stainless steels



Main features of scale in HP steam (Wright & Dooley, 2011)

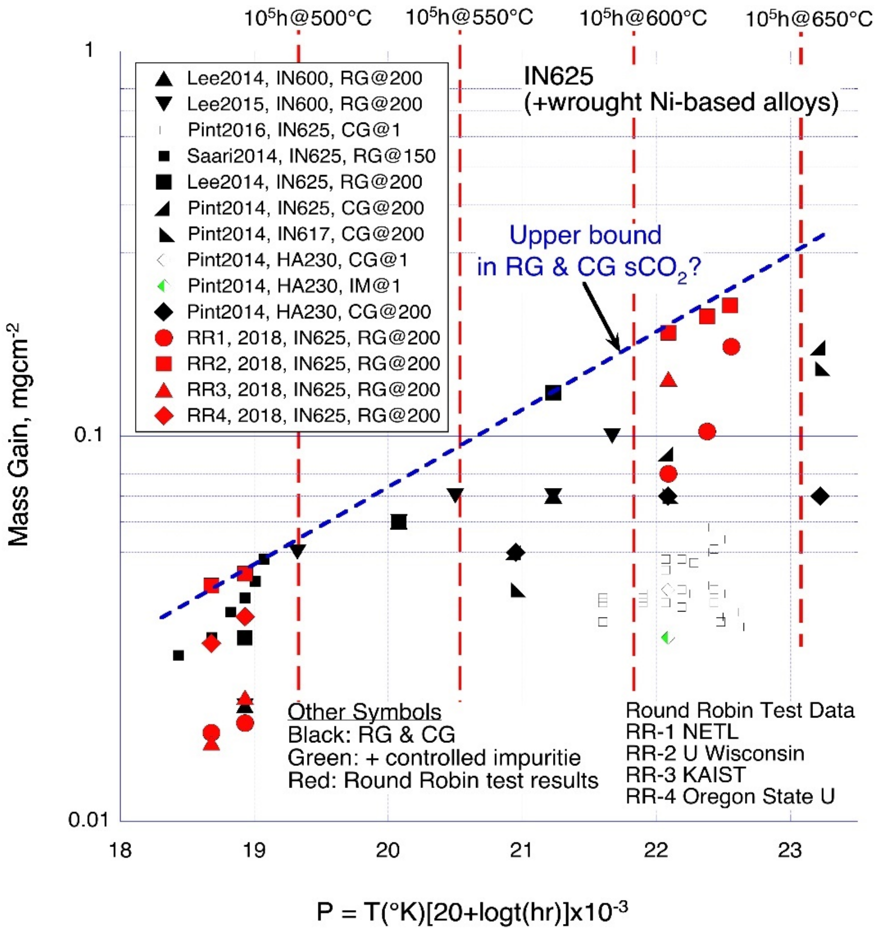


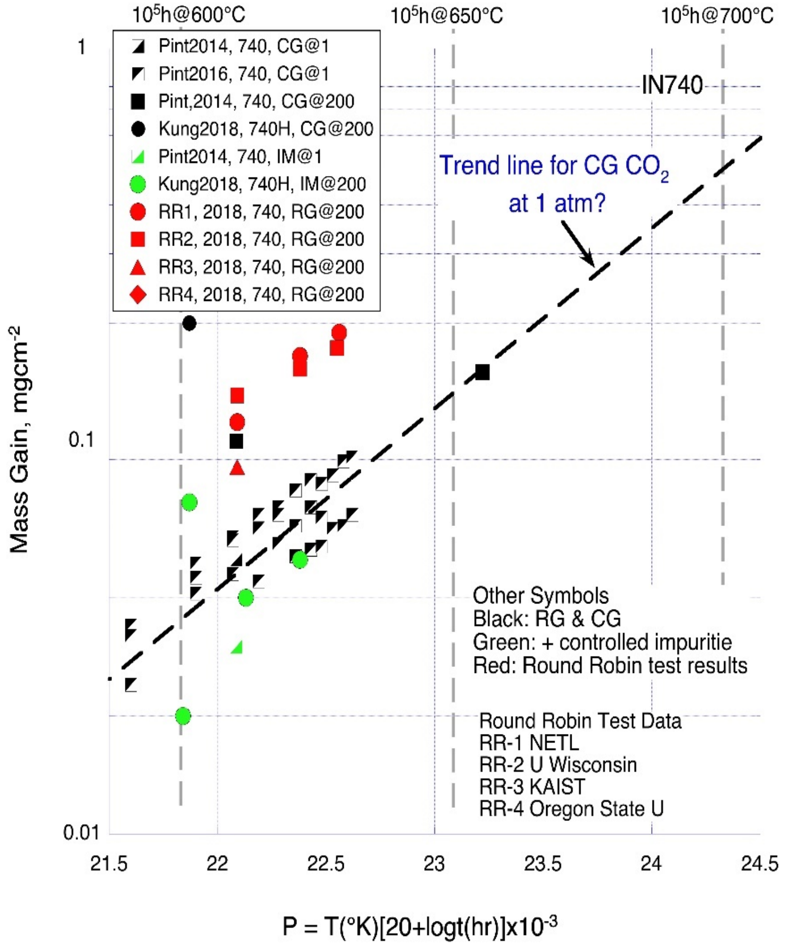
TP347HFG, 11kh at 670°C & 251 bar steam (EPRI Atlas)



TP347HFG, 500h at 700°C & 200 bar CO_2 (Pint & Keiser, 2014)

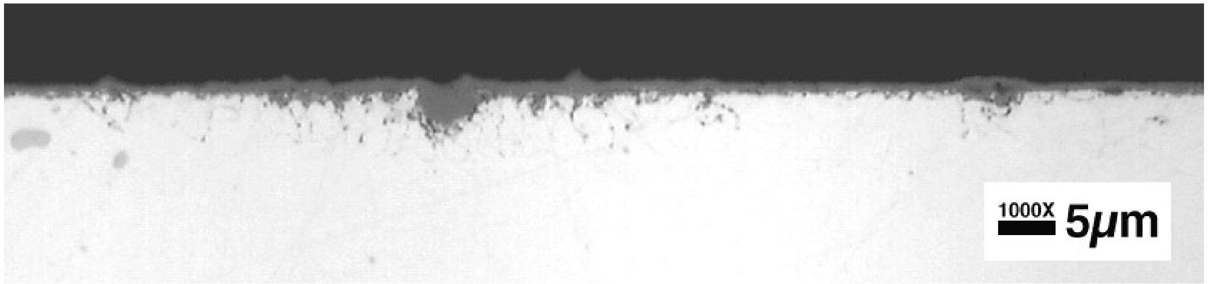
Group 3
HT Ni-base alloys (Cr_2O_3 formers): available data in sCO_2



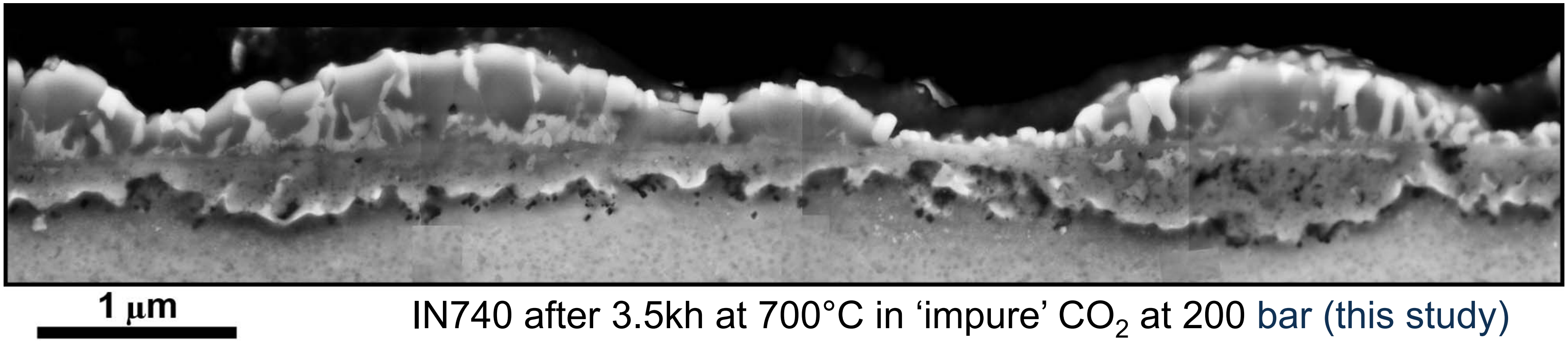


Group 3
Thickness measurements on HT alloys are challenging

- Maximum power of optical microscopy produced marginal resolution



- New SEM/BSE/EDS/EBSD techniques used
  - non-uniform scale clearly evident on 740H surface



IN740 after 3.5kh at 700°C in ‘impure’ CO_2 at 200 bar (this study)

FIB-STEM can offer better resolution but is time consuming and limited in area coverage

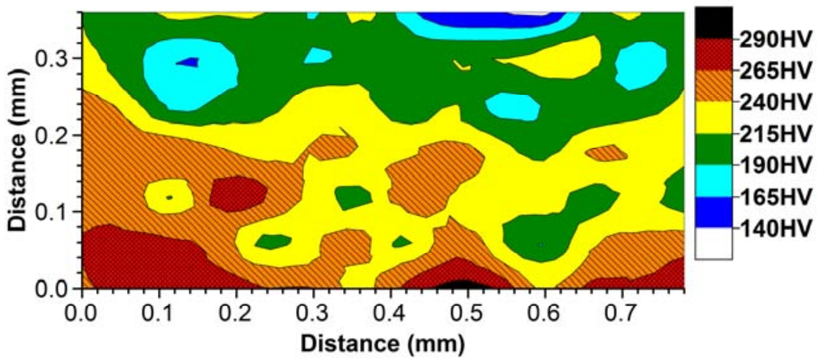
Carburization:
Concern for surface hardening and Cr depletion

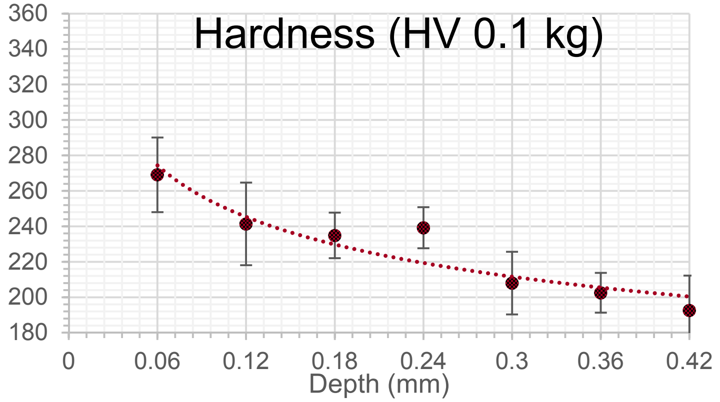
Current Understanding

- Ferritic steels
  - *UK research (1970s) identified breakaway oxidation phenomenon under AGR conditions*
- Austenitic steels
  - *C pick-up observed only in initial stages, or when duplex scales present (or after exfoliation)*
- Cr_2O_3 scales are known to be excellent barriers to C ingress
  - *confirmed by recent observations at 550-750°C, 200 bar (Pint, ORNL)*
- High total Ni+Cr content in alloys is beneficial
- High-Cr Ni-based (HT) alloys are likely to resist carburization
  - *maybe equally applicable to solid solution and precipitation-strengthened Ni-based alloys*

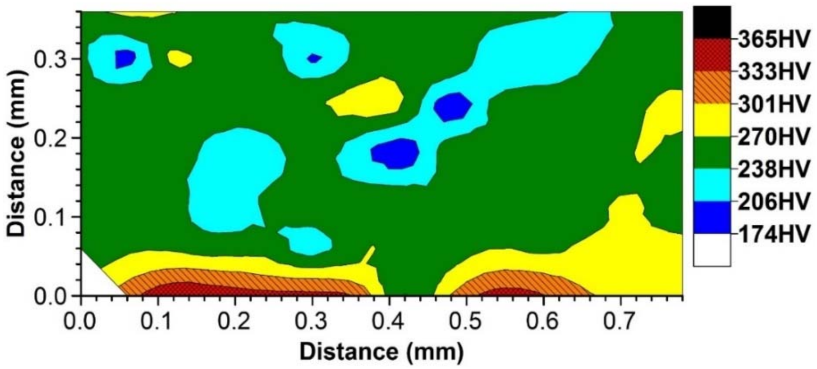
Ferritic steels showed different degrees of surface hardening after 1000h at 700°C in CO_2 -3.6% O_2-5.3% H_2O at 200 bar

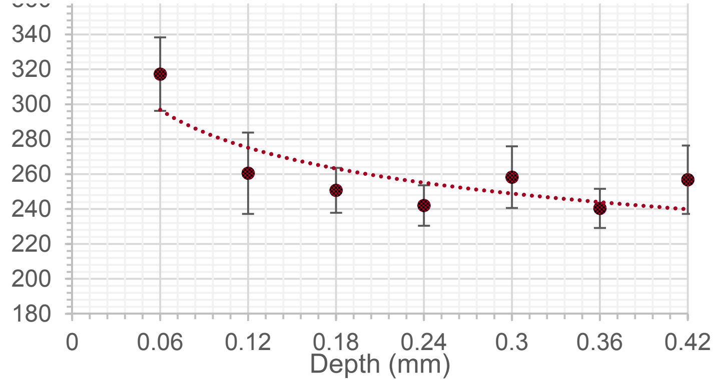
Gr91



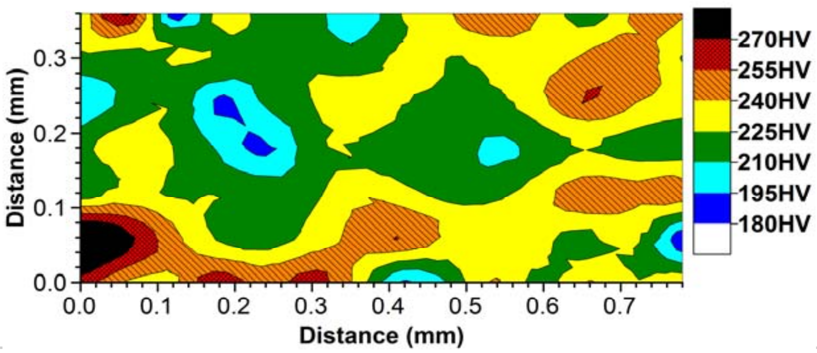


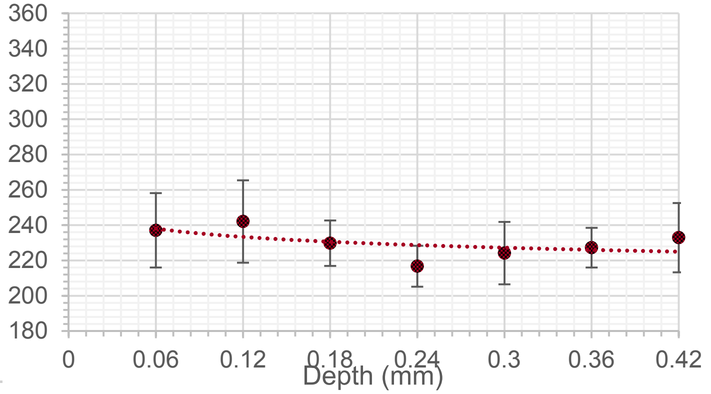
VM12





Crofer 22H





Overall observations on carburization (this study)

- Ferritic steels
  - *expect continuous C uptake until alloy saturation*
  - *oxidizing impurities retard hardening*
- Conventional austenitic steel
  - *TP304H showed initial hardening (after 300h) in* sCO_2 *with oxidizing impurities*
    - *after 1,000h, possibly small increase in overall alloy hardness, but no gradient (consistent with UK AGR results)*
- Reliable Cr_2O_3-forming alloys :
  - *high-Cr austenitic (HR3C): hardening of surface to 150-200 µm*
  - *Ni-base alloys: no evidence of hardening (as expected)*

Modeling:
Thickness-based oxide growth kinetics for sCO_2 corrosion

Focus on three potential failure modes:

1. Reduction of flow area in channels from oxide growth
2. Cr depletion due to oxide formation
3. Time to scale failure (oxide exfoliation/blockage)

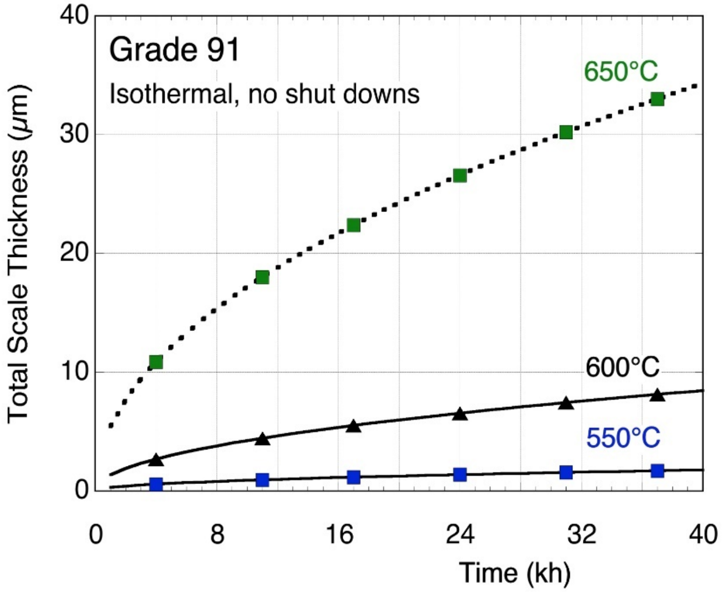
Arrhenius constants used to *modify EPRI Oxide Exfoliation Model*

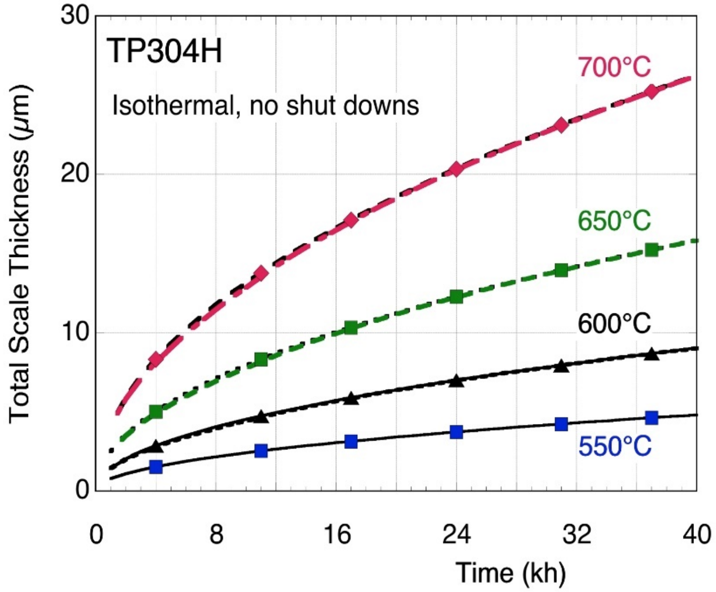
Alloy	T°C	A ($\mu m^2/h$)	Q (kJ/mole)	R^2	Source
Gr91	650-750	2.3×10^{19}	374	0.88	This work
VM12	650, 750	4.1×10^{7}	162	1*	This work
Crofer 22H	650-750	1.2	14**	1*	This work
TP304H	650-750	7.6×10^{5}	148	0.99	This work
HR3C	650-750	NA	NA	—	—
IN617	650-750	NA	NA	—	—
IN740	650-750	NA	NA	—	—
IN740	*650-800*	1.4×10^{5}	*166*	*0.97*	*17 bar steam*
310HCbN	*650-800*	2.3×10^{2}	*112*	*0.98*	*17 bar steam*

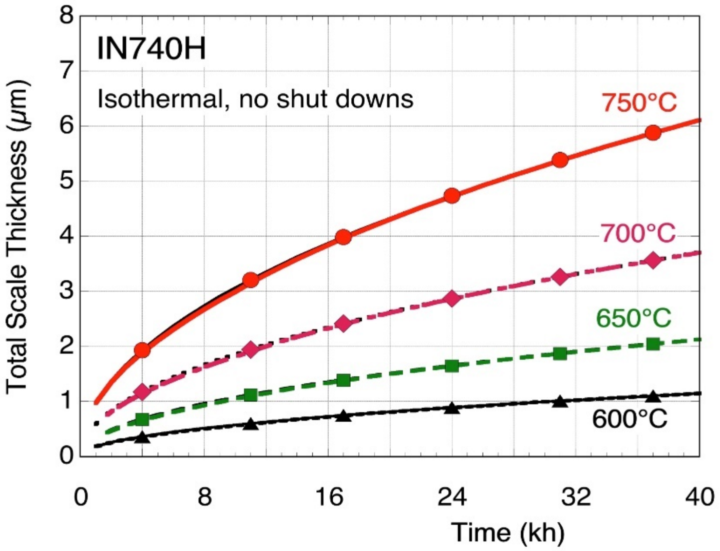
*Two data points only, at 650 and 750°C

**Very unusual T-dependence, possibly associated with a change in the type of scale formed due to rapidly increasing Cr diffusion at the higher temperatures.

Oxide growth in sCO_2 predicted by modified EPRI Oxide Exfoliation Model (isothermal)

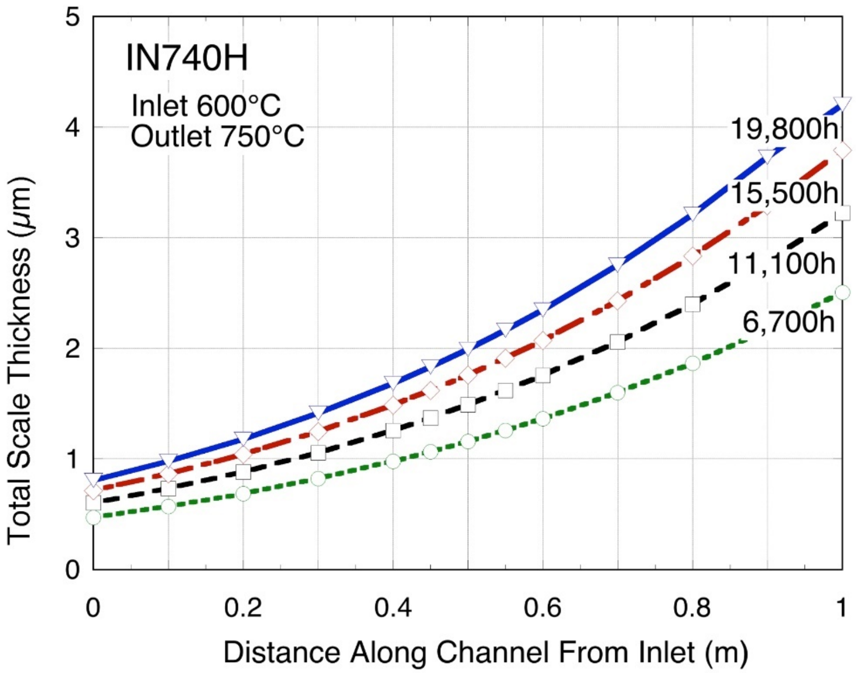


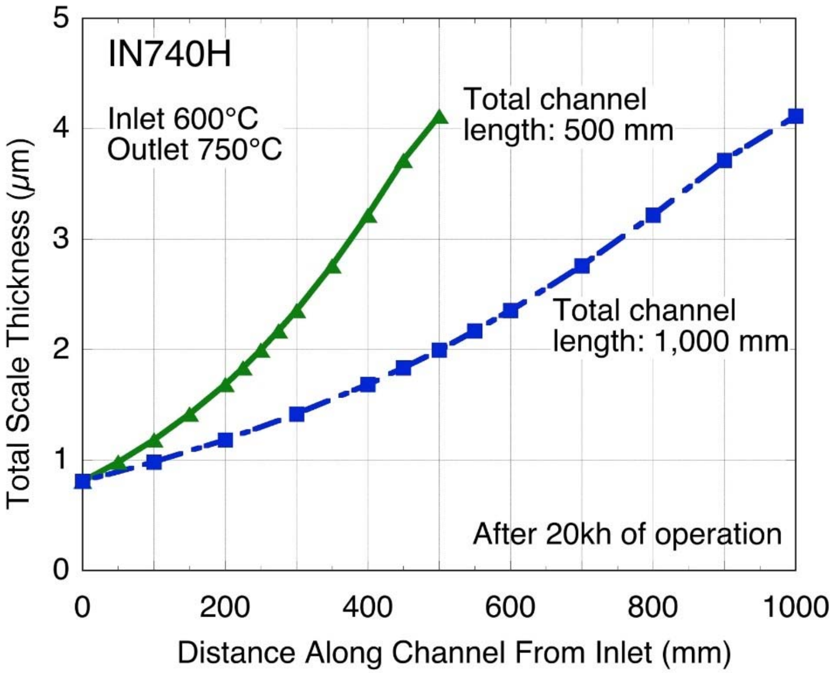




Growth of scale thickness along a compact HX channel

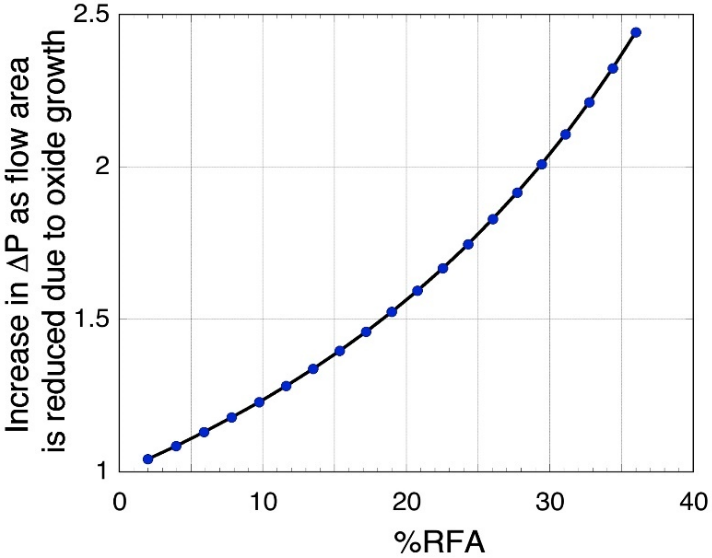
- Local T along a channel dictates the rate of scale growth
  - *hottest end will attain d_{crit} first*
  - *length of channel (for a given ΔT) influences blockage considerations*
- Critical oxide thickness (d_{crit}) is dictated by considerations of:
  - *acceptable reduction in flow area (i.e., pressure drop)*
  - *exhaustion of Cr reservoir (breakaway oxidation)*
  - *scale exfoliation/failure and channel blockage*





Failure mode 1: Reduction in flow area from oxide growth (RFA_{ox})

- Favored designs of sCO_2 recuperators employ small flow channels
  - *ΔP is thus a critical consideration*



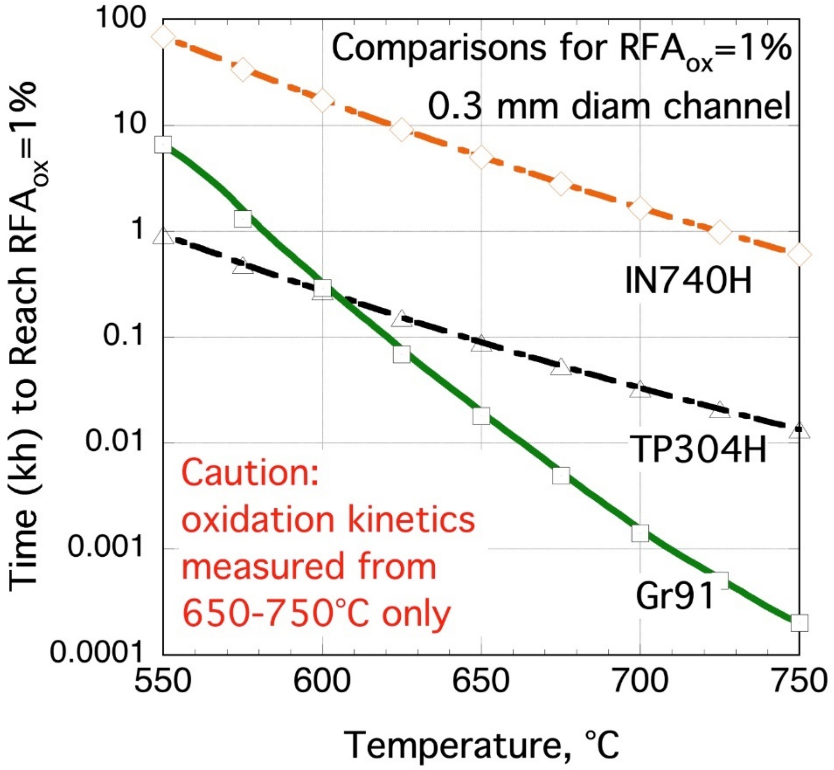
- *shown for laminar flow*
  - *lower ΔP for turbulent flow*
- *RFA of 2-5% typically considered acceptable*

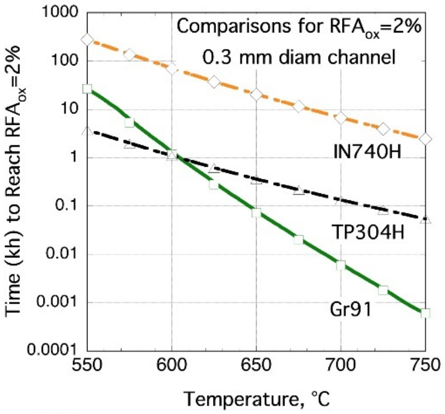
- Rate of oxide growth drives RFA_{ox}
- If RFA_{ox} values of ≥ 5% cannot be tolerated, the resulting d_{crit} is very small

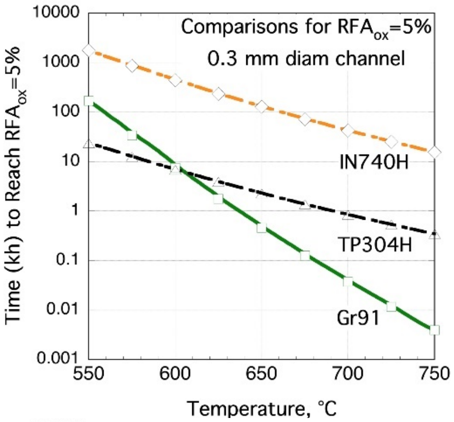
Tube ID (mm)	**Critical Oxide Thickness, d_{crit} (µm)**		
RFA_{ox}:	**1%**	**2%**	**5%**
0.3	0.75	1.5	3.8
0.6	1.5	3.0	7.6
0.9	2.3	4.5	11.4

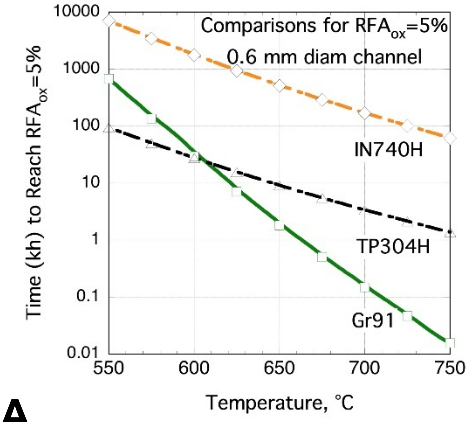
Oxide thicknesses 1-10µm may also impact heat transfer even if scale remains intact

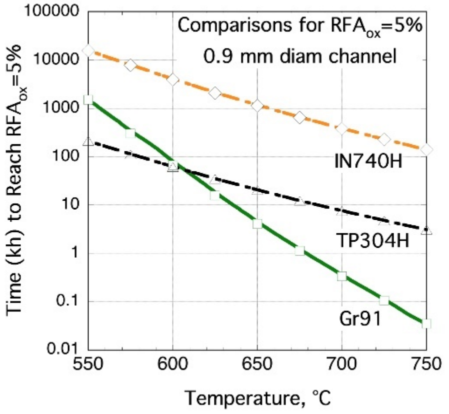
Failure mode 1:
Reduction in flow area by oxide growth occurs rapidly











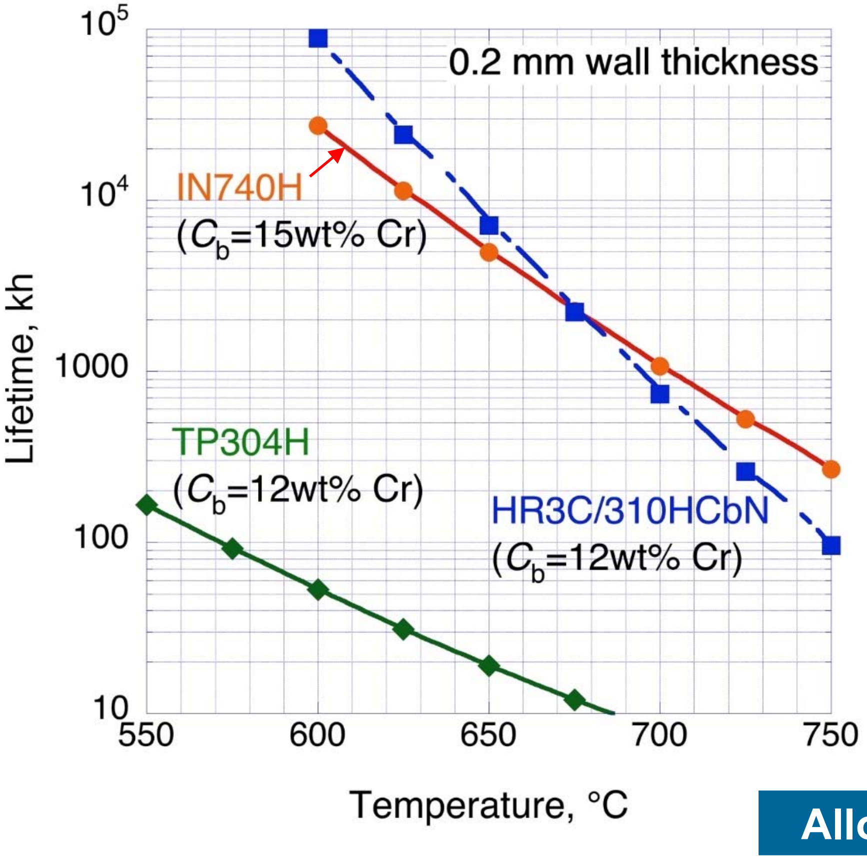
Times (hours) to reach stated %RFA$_{ox}$

Alloy	T°C	0.3 mm Channel ID			0.6 mm	0.9 mm
	RFA$_{ox}$:	1%	2%	5%	5%	5%
Grade 91	**600**	290	1,170	7,390	29,560	66,390
TP304H	**650**	88	357	2,259	9,034	20,292
IN740H	**700**	1,638	6,641	42,060	168,240	377,870

***In terms of lifetime*:**

- 0.3 mm channels are problematic for all alloys
- 1% RFA$_{ox}$ problematic (except for IN740H with 0.9 mm channel ID)

Failure mode 2:
Depletion of Cr reservoir leading to breakaway oxidation



- Model approach validated for conditions where there is no depletion gradient in Cr
  - *for alumina-forming ferritic steels at T >1000°C*
- Where a Cr-depletion gradient exists, critical Cr content (C_b) may be significantly reduced
  - *if, for instance, Cr gradient results in 1.25x assumed C_b, calculated lives would be reduced by a factor of 40-70%*
- New modeling based on this scenario (Duan, et al. 2016) should provide guidance

➢ *Overall, it appears that this scenario is likely to be life-limiting only for TP304H*

NOTE
C_b values estimated from general knowledge.

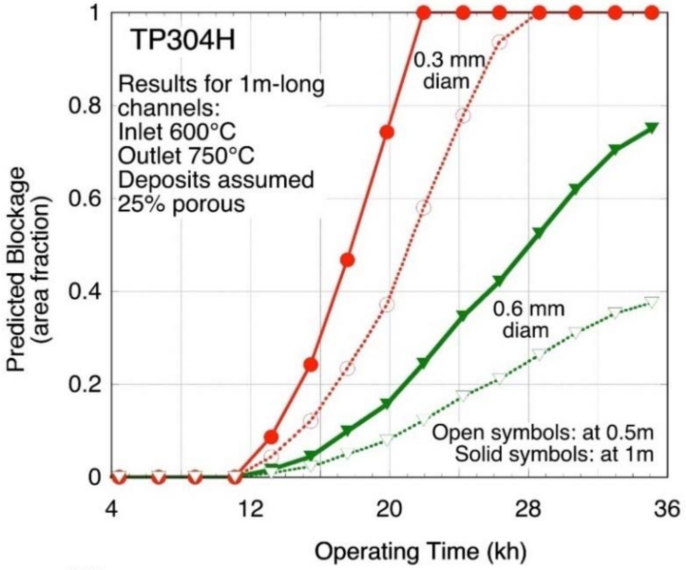
Alloy	T°C	Lifetime, kh			
Wall thickness, mm:		**0.2**	**0.3**	**0.5**	**1.2**
TP304H	**650**	19	43	120	692
HR3C	**700**	739	1,663	4,619	26,605
IN740H	**700**	1,070	2,407	6,686	38,509

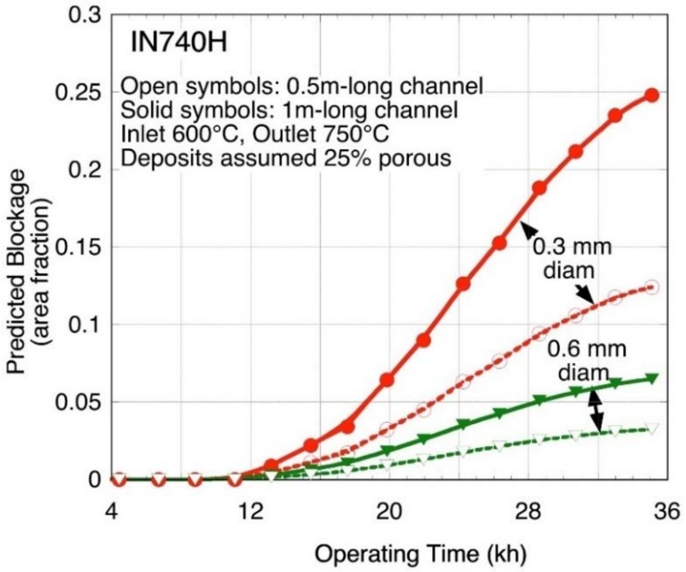
Failure mode 3:
Time to reach critical scale strain for exfoliation

Assumptions:

- Unit is shut down every 3 months
  - *ΔT (ΔP) in shut down provides stress peak/scale failure and exfoliation*
  - *tubes cleaned out*
- Length of accumulated exfoliant = 10x channel diameter
- Blockage (RFA_B) is a discrete event
  - *RFA_{ox} is a function of time*

Alloy	**T°C**	**Lifetime, kh**			
Channel length, m:		**0.5**		**1.0**	
Channel diam, mm:		**0.3**	**0.6**	**0.3**	**0.6**
TP304H	**550-700**	33.9	>>40	30.8	>40
	600-750	13.2	17.5	12.2	15.6
IN740H	**600-750**	22.4	>40	18.7	28.6





'Fate of debris' for thermally grown oxides is not understood for small-channel HX

Summary

- First project to address oxidation in direct-fired sCO_2 Allam cycles (with impurities)
- Oxide growth rates in sCO_2
  - *appear consistent with (and similar to) those in HP steam*
  - *possibly slower when oxidizing impurities are present in sCO_2*
  - *no systematic effect from pressure*
- Scale morphologies
  - *nominally follow expectations for steam oxidation, with some potential influences from C*
- Surface hardening
  - *identified in Gr 91 and VM12; more pronounced in 'pure' sCO_2*
  - *also found in TP304H & HR3C*
  - *none apparent in Ni-base alloys*
- Existing EPRI Oxide Exfoliation Model modified
- Impact of three lifetime-limiting scenarios from scale growth in sCO_2 evaluated
  - **Degree of concern: RFA > exfoliation/blockage > Cr depletion**
  - Model available for corrosion researchers and system designers to use in component design

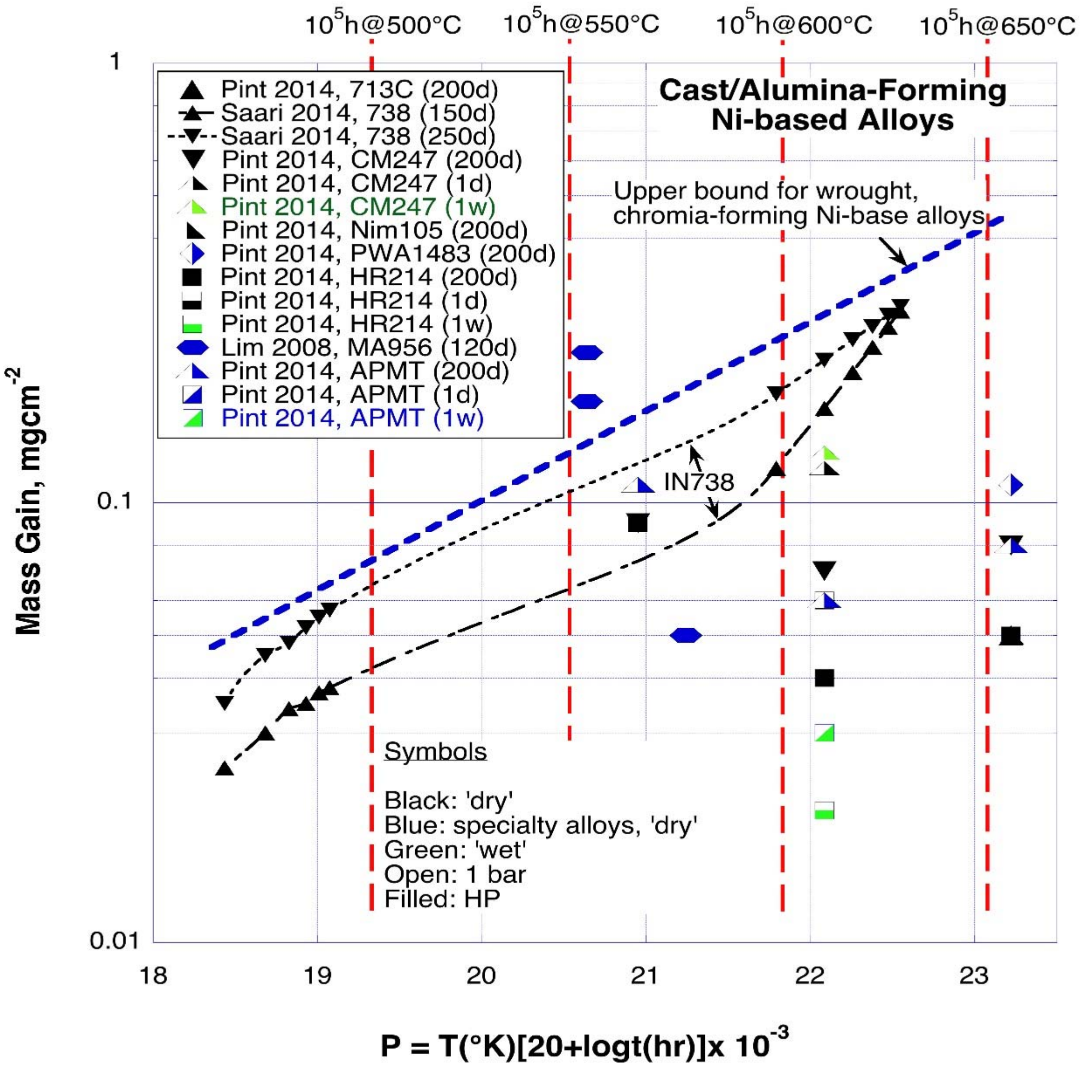
Acknowledgements

This work was sponsored by the DOE Office of Fossil Energy Cross-Cutting Materials Research Program under contract ***DE-FE0024120***

- NETL project manager: Vito Cedro

Together…Shaping the Future of Electricity

Group 4
HT Ni-base alloys (Al_2O_3 formers): available data in sCO_2



- Considerable scattering
- Less protective γ-Al_2O_3 is formed at low T
- Similar growth rates as Cr_2O_3 formers